

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP012254

TITLE: Fabrication of Metal Nanostructures in Mesoporous Silicas

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Nanophase and Nanocomposite Materials IV held in Boston, Massachusetts on November 26-29, 2001

To order the complete compilation report, use: ADA401575

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP012174 thru ADP012259

UNCLASSIFIED

## Fabrication of Metal Nanostructures in Mesoporous Silicas

Kuei Jung Chao and Chia Min Yang

Department of Chemistry, National Tsinghua University

Hsinchu, 300, Taiwan

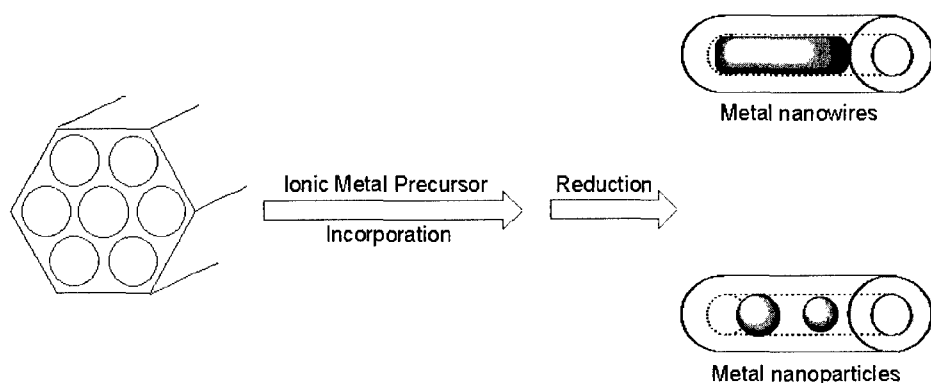
### ABSTRACT

Mesoporous silicas were used as hosts for fabrication of nanostructured metals. Due to the confinement effect, densely packed metal nanowire bundles and nano-networks or highly dispersed metal nanoparticles were prepared inside the channels of mesoporous silicas by metal incorporation/reduction processes. The structure of nanostructured metals was analyzed by TEM and PXRD, and the composition was investigated by ICP-AES, EDX and EELS.

### INTRODUCTION

Metal nanostructures have attracted growing interests recently, because of their unique physical and chemical properties of low dimensionality [1-3]. They could be synthesized within the confined space of a host material. For example, one-dimensional metal nanowire arrays have been synthesized in anodic alumina membrane with diameter of 13-100 nm [1-2,4-5]. To prepare metal nanostructures with even smaller size, ordered mesoporous silicas (*e.g.* MCM-41, MCM-48, SBA-15) with uniform pore diameters (1.5-30 nm) and tunable pore structures are considered to be promising hosts [6-8].

One advantage of mesoporous silica over other templates is the feasibility of modification of the pore walls to have desired properties [9-11]. In this report, we show that various metal nanostructures can be synthesized in the mesoporous silica hosts by following the process shown in figure 1. Preparations of various metal nanostructures including densely packed metal nanowire bundles and nano-networks or highly dispersed metal nanoparticles are demonstrated. Their structures as well as compositions were analyzed.



**Figure 1.** Schematic representation of fabrication of metal nanostructures in MCM-41.

## EXPERIMENTAL

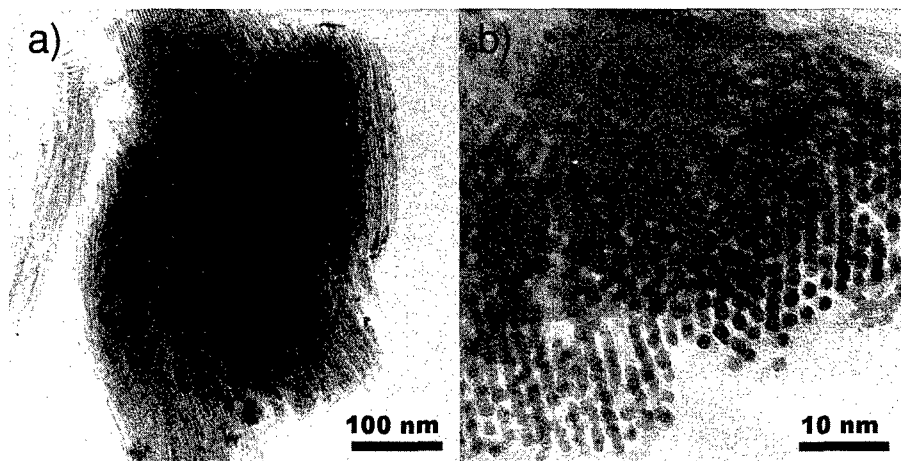
Siliceous MCM-41 with one-dimensional channels and hexagonal symmetry as well as MCM-48 with bicontinuous channels and cubic symmetry were synthesized according to some known procedures [12-13]. The organic templates were removed by calcination at 813 K for 6 hours in airflow. Ionic metal precursors were incorporated on the intrachannel surface of calcined and modified mesoporous silica, and were then reduced to form metal/ silica composites in hydrogen flow at 373-573 K.

The pore diameter and the pore volume of calcined MCM-41 and MCM-48 were determined by Barrett-Joyner-Halenda (BJH) method from nitrogen sorption isotherm. The powder X-ray diffraction (PXRD) was performed to determine the structure and the periodicity of the pores in host silicas. The pore wall thickness can be deduced from the pore diameter in combination with PXRD analysis. The metal content in the reduced metal/silica composite was mainly determined by inductively coupled plasma (ICP) analysis. The peak widths of PXRD of nanostructured metals were used to estimate the average crystalline domain size of the metal in the composite by a spherical model and Scherrer's equation. The data was compared with the images from transmission electron microscope (TEM). Energy-dispersive X-ray (EDX) analysis as well as Electron energy loss spectroscopy (EELS) were also performed for compositional studies.

## RESULTS AND DISCUSSION

The Pt content of Pt/MCM-41 composite was ~40 wt% as determined by ICP analysis. The PXRD pattern of the composite indicates the existence of both the hexagonal structure of MCM-41 (small-angle region) and face-centered cubic structure of Pt metal (wide-angle region). Figure 2 shows the TEM images of the composite, which indicate that almost all the channels of MCM-41 were filled with Pt, resulting in densely packed Pt nanowire bundles with quasi-hexagonal symmetry. Few discrete Pt particles were found inside the MCM-41 due to the collapse and defects of MCM-41 formed during calcination. The diameters of Pt nanowires were uniform in size (2.1 nm), as determined by PXRD and TEM, smaller than the pore diameter of MCM-41 (2.4 nm). The lengths of Pt nanowires were several hundred nanometers in average as estimated from TEM images, occupying about 40-70% of the channel length of MCM-41 as calculated from nitrogen sorption isotherm. The aspect ratio of these nanowires was generally over 100. EDX analysis of the nanowire region of Pt/MCM-41 composite revealed the Pt to Si ratio of 0.5, consisting with the result of ICP analysis. The TEM images of ultra-microtomed composites suggest that the Pt nanowires may have preferred direction of growth in the channels of MCM-41.

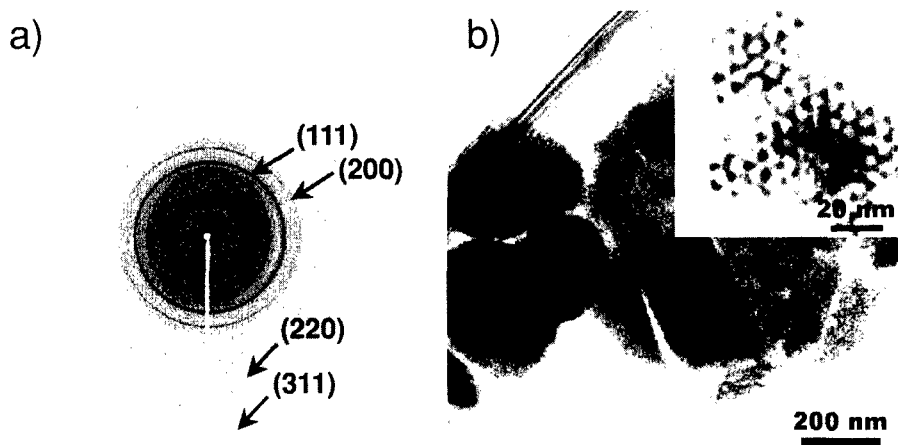
Alternatively, MCM-48 was used to incorporate Pt to form metal nano-networks. The



**Figure 2.** TEM images of Pt/MCM-41 composite perpendicular (a) and along (b) the hexagonal axis of MCM-41.

Pt/MCM-48 composite was filled in a capillary tube for PXRD measurements. Fig. 3a shows the PXRD ring pattern of the composite. Each diffraction ring of Pt is broad and weak in intensity, with no discernable diffraction spots in the rings. This suggests that most of Pt metals were small in size and stayed in the pores of MCM-48 after reduction. It may be due to the tortuous nature of the host MCM-48, preventing further ordered stacking in the confined space. The TEM image of Pt/MCM-48 (figure 3b) shows that all MCM-48 particles were filled with Pt metals, and the Pt nano-networks were densely packed inside the host MCM-48. The images of Pt nano-networks reflect the structure of the pore system of MCM-48 (inset of figure 3b) with 1a3d symmetry. EDX analysis revealed Pt to Si ratio similar with that of Pt/MCM-41. Because the channels of MCM-48 are bicontinuous and connected, unsupported Pt nanowire networks could be obtained after removal of the silica template by HF solution.

The same protocol can also be used to prepare other metal nanostructures. For example, palladium nanowires bundles in MCM-41 as well as gold nano-networks in MCM-48 can be prepared. In addition, our strategy to fabricate densely packed metal nanostructures can be applied to synthesize metal nanoparticles in mesoporous silicas. Uniform sized and highly dispersed Pt nanoparticles were formed in the channels of MCM-41 by controlling the loading amount of metal precursors. The Pt loading was determined by ICP analysis to be 3-11 wt%, depending on the metal loading. The supported and uniform Pt nanoparticles in MCM-41 with controlled metal loading and morphology may be useful in catalysis. By *in-situ* TEM



**Figure 3.** (a) PXRD ring pattern of Pt/MCM-48 composite. (b) TEM image of ultramicrotomed Pt/MCM-48 composite. The inset shows the thin edge of the composite.



**Figure 4.** *In-situ* TEM images of Pt/MCM-41 composite at room temperature (a), 200°C (b) and 600°C (c).

investigation under 10 mbar hydrogen atmosphere, Pt nanoparticles formed after hydrogen reduction at 200°C were found to be extremely stable in the confined channels. No relative movements to the host silica were observed even after heating to 600°C (figure 4). EELS analysis showed the existence of platinum as well as trace of carbon in the composite. The unusual thermal stability of Pt nanoparticles in MCM-41 may be attributed to the host confinement effect as well as the interaction of Pt with the silica walls.

## CONCLUSIONS

In summary, the formation of metal nanostructures in mesoporous silicas has been demonstrated. The structural analyses confirm the nanocrystalline nature of the densely packed metal wire bundles and networks as well as highly dispersed metal particles. Highly dispersed Pt nanoparticles were found to have very good thermal stability inside the confined space of MCM-41.

## ACKNOWLEDGEMENTS

We wish to thank the assistance of Dr. H. S. Sheu at Synchrotron Radiation Research Center, Hsinchu, Taiwan in XRD measurements, and Dr. S. Helveg and Dr. P. L. Hansen at Haldor Topsøe A/S, Lyngby, Denmark in *in-situ* TEM investigations.

## REFERENCES

1. T. M. Whitney, J. S. Jiang, P. C. Searson, C. L. Chien, *Science* **261**, 1316 (1993).
2. Z. Zhang, J. Y. Ying, M. S. Dresselhaus, *J. Mater. Res.* **13**, 1745 (1998).
3. M. Sasaki, M. Osada, N. Sugimoto, S. Inagaki, Y. Fukushima, A. Fukuoka, M. Ichikawa, *Microporous Mesoporous Mater.* **21**, 597 (1998).
4. C. R. Martin, *Science*, **266**, 1961 (1994).
5. B. R. Martin, D. J. Dermody, B. D. Reiss, M. Fang, L. A. Lyon, M. J. Natan, T. E. Mallouk, *Adv. Mater.* **11**, 1021 (1999).
6. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **359**, 710 (1992).
7. Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, G. D. Stucky, *Nature* **368**, 317 (1994).
8. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **279**, 548 (1998).
9. Y. Shin, J. Liu, L. Q. Wang, Z. Nie, W. D. Samuels, G. E. Fryxell, G. J. Exarhos, *Angew. Chem. Int. Ed.* **39**, 2702 (2000).
10. H. Fan, Y. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, V. Perez-Luna, G. P. López, C. J. Brinker, *Nature* **405**, 56 (2000).
11. A. Stein, B. J. Melde, R. C. Schroden, *Adv. Mater.* **12**, 1403 (2000).
12. Q. Cai, W. Y. Lin, F. S. Xiao, W. Q. Pang, X. H. Chen, B. S. Zou, *Microporous Mesoporous Mater.* **32**, 1 (1999).
13. R. Ryoo, S. H. Joo, J. M. Kim, *J. Phys. Chem. B* **103**, 7435 (1999).